

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup>:</b> C08G 18/38, 18/67	<b>A1</b>	<b>(11) International Publication Number:</b> WO 95/02004 <b>(43) International Publication Date:</b> 19 January 1995 (19.01.95)
<b>(21) International Application Number:</b> PCT/NL94/00155 <b>(22) International Filing Date:</b> 5 July 1994 (05.07.94)  <b>(30) Priority Data:</b> 08/089,173      8 July 1993 (08.07.93)      US 08/212,265      14 March 1994 (14.03.94)      US  <b>(71) Applicant:</b> DSM N.V. [NL/NL]; Hct Overloon 1, NL-6411 TE Heerlen (NL).  <b>(72) Inventors:</b> BISHOP, Timothy, E.; 1720 Riverwood Drive, Algonquin, IL 60102 (US). POKLACKI, Erwin, S.; 1223 South Fernandez, Arlington Heights, IL 60005 (US).  <b>(74) Agent:</b> KLEIBORN, Paul, Erik; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).		<b>(81) Designated States:</b> AU, CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> HALOGEN-FREE RADIATION CURABLE FLAME RETARDANT COMPOSITIONS		
<b>(57) Abstract</b>  A halogen-free radiation curable flame retardant composition that comprises an end-capped oligomer of a phosphonate polyol and a polyisocyanate and an organic monomer.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

HALOGEN-FREE RADIATION CURABLE  
FLAME RETARDANT COMPOSITIONS

5

Technical Field of the Invention

This invention relates to halogen-free radiation curable polyurethane resin compositions containing  
10 phosphonate esters. This invention also relates to halogen-free flame retardant polyurethane compositions.

Background of the Invention

Radiation curable polyurethane resins are widely  
15 used in radiation curable coating compositions for various substrates. Because polyurethane resins are generally flammable, flame retardants must be incorporated in the resins for many applications. However, traditional flame retardants typically contain halogens or require halogens  
20 in their manufacture. For example, flame retardant modified ultraviolet curable urethane acrylate resins with monomers containing bromine and phosphorus have been reported by W. Guo in the Journal of Polymer Science, Part A: Polymer Chemistry, Vol. 30, pp. 819-827 (1992).

25 To avoid the toxic and corrosive combustion products associated with the use of halogens, research efforts are presently directed toward developing radiation curable, halogen-free flame retardant coatings. It has been reported that a phosphonate compound having a  
30 polymerizable vinyl group can be attached by radiation curing to an acrylated, aliphatic polyester urethane. While the compound is an improvement over the halogen-containing flame retardants, the manufacture of the compound requires an acyl halide to form the vinyl group  
35 and produces hydrogen chloride as a manufacturing by-product. Both of these halide compounds present handling and disposal problems.

A need exists for a radiation curable composition that contains no halogens, is manufactured without halide compounds and produces a halogen-free, flame retardant polyurethane resin polymer.

- 5 Preferably, the radiation curable composition would produce a flame retardant polymer which resists leaching by organic chemicals such as acetone and exhibits relatively low thermal weight loss. It would also be desirable to produce a flame retardant polymer that is  
10 optically clear, which excludes the use of inorganic fillers such as hydrated alumina, magnesium hydroxide or antimony oxide.

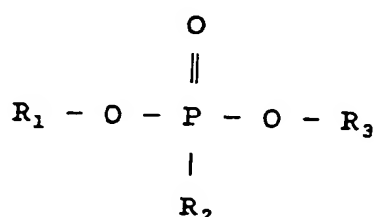
- One application for such a composition is the matrix material in optical fiber plenum cables. The  
15 flammability requirements for plenum cables are very stringent and difficult to meet without a flame-retardant matrix material. A matrix is a composition that covers or coats a group of optical fibers. Typically, the group consists of about 4 to about 8 optical fibers; however,  
20 the group may consist of more than 8 or less than 4 optical fibers. The matrix is used to help bond the optical fibers together and protect the fibers from environmental stress even though the optical fibers may already be individually coated with various coatings. A  
25 clear, non-halogenated, radiation curable matrix material provides for easy visibility of the optical fibers, low corrosivity of combustion products, and fast line speeds.

#### Summary of the Invention

- 30 This invention relates to a radiation curable composition essentially without halogens that is suitable for producing flame retardant polymers. The composition comprises an end-capped oligomer of a phosphonate polyol and a polyisocyanate, a monomer susceptible to free  
35 radical copolymerization, and, optionally, a photoinitiator.

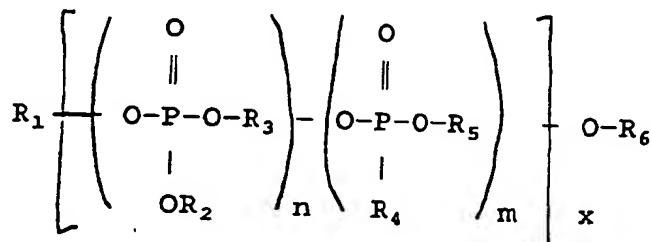
In one embodiment, the invention is a radiation

curable composition that comprises an oligomer of a polyisocyanate and a phosphonate polyol, the oligomer being end-capped by at least one monohydroxy acrylate, and an organic monomer capable of participating in a free radical copolymerization with the end-capped oligomer. The composition may also contain a photoinitiator that is sensitive to ultraviolet electromagnetic radiation. Generally, the polyol is of the formula:



wherein  $\text{R}_1$  and  $\text{R}_3$  are independently  $\text{C}_1$  to  $\text{C}_{18}$  alkyl or aryl; and  $\text{R}_2$  is polyhydroxyalkyl, polyhydroxyaryl, polyhydroxyalkylaminoalkyl, polyhydroxyarylaminoalkyl, polyhydroxyalkylaminoaryl or polyhydroxyarylaminoaryl having from 1 to 18 carbon atoms inclusive.

In another embodiment, the invention is a radiation curable composition essentially free of halogens that comprises an oligomer which is the reaction product of a polyisocyanate and a phosphonate polyol, said oligomer being capped by at least one monohydroxy functional compound with ethylenic unsaturation, and said polyol having the formula:



wherein  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_4$  and  $\text{R}_6$  are each independently selected from the group consisting of alkyl, aryl, poly (alkylene oxide) polyhydroxyalkyl, polyhydroxyaryl,

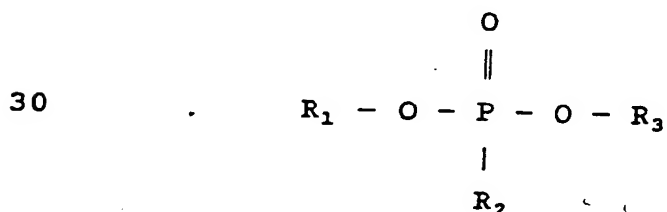
polyhydroxyalkylaminoalkyl, polyhydroxyarylaminoalkyl,  
polyhydroxyalkylaminoaryl and polyhydroxyarylaminoaryl;  $R_3$   
and  $R_5$  are each independently selected from the group  
consisting of alkylene and arylene;  $m$  and  $n$  are each  
5 independently an integer from 0 to 10 inclusive, provided  
that at least one of  $m$  and  $n$  is 1 or more; and  $x$  is 1 to  
100.

The composition also comprises an essentially  
halogen-free organic monomer. The composition may also  
10 contain a photoinitiator that is sensitive to ultraviolet  
electromagnetic radiation.

#### Detailed Description of the Invention

This invention provides a radiation curable  
15 composition suitable for use in producing a flame  
retardant polymer. The composition comprises an end-capped  
oligomer of a phosphonate polyol and a polyisocyanate. As  
used herein the term "polyisocyanate" shall mean a  
molecule having one or more isocyanate functional groups.  
20 The composition also contains a halogen-free organic  
monomer and, optionally, a photoinitiator.

In one aspect, the invention is a composition  
which comprises an oligomer of a phosphonate polyol and a  
polyisocyanate. Preferably, the polyol is a diol and the  
25 isocyanate is a diisocyanate. Preferred polyols have the  
formula



wherein  $R_1$  and  $R_3$  are independently  $C_1$  to  $C_{18}$  alkyl or aryl;  
35 and  $R_2$  is polyhydroxyalkyl, polyhydroxyaryl,  
polyhydroxyalkylaminoalkyl, polyhydroxyarylaminoalkyl,  
polyhydroxyalkylaminoaryl or polyhydroxyarylaminoaryl

having from 1 to 18 carbon atoms inclusive.

As used herein, the term "alkyl" refers to a straight or branched group of 1 to 18 carbon atoms inclusive including, but not limited to, methyl, ethyl, n-  
5 propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl and the like.

As used herein, the term "aryl" includes aromatic rings that are fused, unfused or linked that can contain up to 18 carbon atoms and can include one or more  
10 hetero atoms, as for example, phenyl, naphthyl, anthracenyl, biphenyl, quinolyl and the like. The aromatic rings can be unsubstituted or substituted with alkyl groups.

As used herein, the term "poly(alkylene oxide)"  
15 means a series of alternating alkyl groups and oxygen atoms. Examples of poly(alkylene oxides) include, but are not limited to polyethylene oxide, polypropylene oxide, and polybutylene oxide.

As used herein, the term "polyhydroxyalkyl"  
20 means an alkyl group having one or more hydroxyl (-OH) functional groups.

As used herein, the term "polyhydroxyaryl" means an aryl group having one or more hydroxyl functional groups.

25 As used herein, the term "polyhydroxyalkylaminoalkyl" means an alkyl group that is attached to an amino group, and the amino group is substituted with at least one alkyl group having one or more hydroxyl functional groups.

30 As used herein, the term "polyhydroxyarylaminoalkyl" means an aryl group that is attached to an amino group, and the amino group is substituted with at least one alkyl group having one or more hydroxyl functional groups.

35 As used herein, the term "polyhydroxyarylaminoaryl" means an aryl group that is attached to an amino group, and the amino group is

substituted with at least one aryl group having one or more hydroxyl functional groups.

An example of a preferred polyol is diethyl-N,N-bis(2-hydroxyethyl)aminomethyl phosphonate, which is commercially available from Akzo Chemicals, Inc. of Chicago, Illinois under the trade name FYROL<sup>™</sup> 6.

Phosphonate polyols are preferred over phosphate polyols since the former are believed to be relatively more resistant to hydrolysis than are phosphate polyols.

The reaction of polyisocyanates with polyols to produce oligomers containing the urethane group is well known and need not be described in detail here. Preferably, the polyisocyanate is a diisocyanate. Suitable diisocyanates include, but are not limited to, toluene diisocyanate, isophorine diisocyanate, trimethylhexane diisocyanate, dicyclohexylmethane diisocyanate, diphenylmethanediisocyanate, hexamethylene diisocyanate, naphthalene diisocyanate, phenylene diisocyanate and diphenyldiisocyanate. Trimethylhexane diisocyanate is most preferred.

The oligomer can be end-capped in many ways. For example, an end-capped oligomer may be made by pre-reacting a diisocyanate with a capping agent to form a monoisocyanate, which is later reacted with a polyol. Alternatively, a polyol, polyisocyanate and capping agent may be reacted together at once, or a polyol and polyisocyanate may be reacted first and the oligomer end-capped subsequently. The reaction of the capping agent with a polyisocyanate produces a stable reaction product which persists in the oligomer until stimulated by the presence of free radicals.

Preferably, the capping agent is a monohydroxy acrylate, such as hydroxymethyl acrylate, hydroxyethyl acrylate, hydroxypropyl acrylate or hydroxybutyl acrylate. A preferred monohydroxy functional acrylate is 2-hydroxyethyl acrylate. Other monohydroxy, ethylenically unsaturated capping agents can also be employed.



These include the corresponding methacrylate, vinyl ether, allyl ether, vinyl ester, itaconate, crotonate compounds and the like.

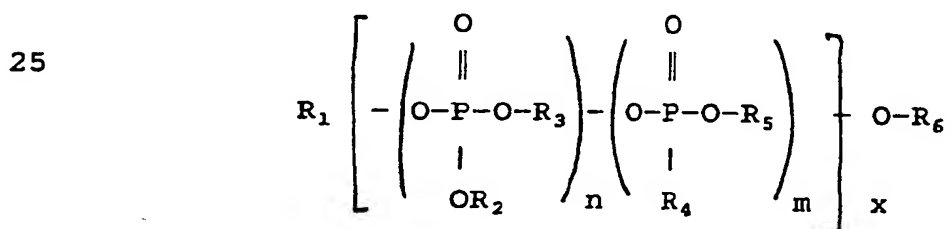
If the amounts of the polyol and the polyisocyanate are relatively close to a stoichiometric balance when the oligomer is synthesized, the oligomer produced tends to have a greater molecular weight. Similarly, polyols of greater molecular weight generally react to produce oligomers of greater molecular weight. These two factors are preferably controlled to provide an end-capped oligomer having a number average molecular weight in the range of about 1,000 to about 3,000.

The oligomer is admixed with an organic monomer. Monomers of higher polarity are more soluble with the polyphosphonate urethane acrylate (i.e. the end-capped oligomer) than are monomers of lower polarity. The monomer contains a functional group that can undergo free radical polymerization, preferably an acrylic or vinylic group. Preferred organic monomers include, but are not limited to, tetrahydrofurfuryl acrylate, ethoxyethoxyethyl acrylate, diethyleneglycol diacrylate, trimethylolpropane ethoxylate triacrylate, methoxyethyl acrylate and hydroxy functional caprolactone acrylate. Preferably, the monomer contains essentially no halogens.

If the composition is to be cured by ultraviolet radiation, a photoinitiator is added to the mixture of the oligomer and organic monomer to induce a free radical reaction involving the oligomers and the monomers on exposure to ultraviolet light. While many such photoinitiators are well known, it is preferred that the photoinitiator contain essentially no halogens. Several suitable photoinitiators are specified in U.S. Patent No. 4,591,522 to Kang et al., which is hereby incorporated by reference. An example of a preferred photoinitiator is 1-hydroxycyclohexylphenylketone. Also preferred is a blend of equal amounts of 2-hydroxy-2-methyl-1-phenylpropane-1-one and 2,4,6-trimethylbenzoyldiphenylphosphine oxide. The

composition may also be cured by various other methods known to those skilled in the art. For, example, curing may be accomplished by exposure of the composition to an electron beam or by thermal means. The composition can, optionally, contain additional components such as stabilizers, plasticizers, adhesion promoters and chain transfer agents.

In another embodiment of the invention, the preferred phosphonate polyol is a water soluble hydroxyl-containing oligomeric phosphonate commercially available from Akzo Chemicals, Inc. of Chicago, Illinois under the trade name FYROL™ 51. This material is prepared from dimethyl methylphosphonate, phosphorous pentoxide, and ethylene oxide. For example, a water soluble hydroxyl-containing oligomeric phosphonate polyol may be made from the reaction product of dimethyl methylphosphonate, phosphorous pentoxide, ethylene oxide and water in a molar ratio of 2:2:8:1, respectively. In general, polyols made from these compounds may have alternating, random or block structures, with the primary components being phosphate and phosphonate groups. The polyol is believed to have the general formula:



wherein  $R_1$ ,  $R_2$ ,  $R_4$  and  $R_6$  are each independently selected from the group consisting of alkyl, aryl, poly (alkylene oxide) polyhydroxyalkyl, polyhydroxyaryl, polyhydroxy-alkylaminoalkyl, polyhydroxyarylaminoalkyl, polyhydroxy-alkylaminoaryl and polyhydroxyarylaminoaryl;  $R_3$  and  $R_5$  are each independently selected from the group consisting of alkylene and arylene;  $m$  and  $n$  are each independently an integer from 0 to 10 inclusive, provided that at least one

- 9 -

of m and n is 1 or more; and x is 1 to 100.

The composition also comprises an essentially halogen-free organic monomer that is polymerizable by a free radical mechanism. The monomer, is for example, 5 diethyleneglycol diacrylate, tripropylene glycol diacrylate, hexanediol diacrylate tetrahydrofurfuryl acrylate, methoxyethyl acrylate, ethoxyethoxyethyl acrylate or trimethyloxypropane triacrylate. The composition can also optionally contain a photoinitiator, 10 as described above. Stabilizers, plasticizers, adhesion, promoters, and chain transfer agents may also be present in the solution.

The halogen-free radiation curable flame retardant compositions of the present invention may be 15 applied to a substrate and cured. As used herein, a substrate shall mean any substance, material, device, etc., on which it is desired to apply a curable composition. The composition may be applied to the surface of the substrate or the composition may be introduced into 20 a substrate, as is the case when the substrate is porous or fibrous or when the substrate has a region in which the composition may be contained. A substrate could, for example, be an electrical circuit board, an optical fiber or a group of optical fibers, or a fibrous material that 25 is part of a composite to be formed. Typically, the composition is applied to a substrate and then the composition is cured. It is contemplated that a substrate may be coated with more than one composition. When a substrate has more than one coating, the coatings may be 30 the same or different, and the coating compositions may be applied sequentially and then all cured at once or each composition may be applied and cured before the next composition is applied.

The following examples are presented to better 35 communicate the invention. The examples are not intended to limit the scope of the invention in any way.

## EXAMPLES

### Example I

An oligomer was prepared by reacting 302.53 g  
5 FYROL™ 51 with the reaction product of 108.90 g of  
trimethylhexane diisocyanate and 59.79 g of 2-  
hydroxyethylacrylate, 0.12 g of phenothiazine, as an  
inhibitor, and 0.20 g dibutyltin dilaurate, a catalyst,  
are also present.

10 The reaction is carried out between 30° and 80°C in the  
presence of an atmosphere of dry air.

The resulting oligomer was clear and colorless  
with a viscosity of 305,000 millipascal-seconds, and had a  
refractive index of 1.477.

15

### Example II

A sample weighing 76.0 g of the oligomer  
prepared in Example I and 20.0 g of hexanediol diacrylate  
were blended to form a solution. To the solution was added  
20 3.0 g of 1-hydroxycyclohexyl phenylketone, 0.5 g of bis(1-  
octoxy-2,2,6,6-tetramethyl-4-piperidinyl)sebacate, and 0.5  
g of thiodiethylene bis(3,5-di-t-butyl-4-  
hydroxy)hydrocinnamate. The sebacate and the  
hydrocinnamate acted as stabilizers. The solution  
25 exhibited a viscosity of 7690 millipascal-seconds. The  
solution was subsequently irradiated with ultraviolet  
light to produce a polymer.

The polymer appeared clear with a straw color  
and was flexible. The polymer proved to be immediately  
30 self-extinguishing in horizontal and vertical flammability  
tests. In each of the tests, a film of the polymer having  
a thickness of 250 microns was exposed to an open flame  
for five seconds. Only minimal smoke was observed.

### 35 Example III

An oligomer was prepared by reacting a mixture  
of 203.12 g FYROL™ 51 and 22.56 g of trimethylol propane

- 11 -

with the reaction product of 96.52 g of 2-hydroxyethyl acrylate and 175.97 g of trimethylhexane diisocyanate. The reactions were carried out between 25° and 90°C in the presence of dry air, 0.13 g of phenothiazine, as an inhibitor, and 0.26 g of dibutyltindilaurate, the catalyst. The resulting oligomer was clear and exhibited a viscosity of greater than 1 million millipascal-seconds.

#### Example IV

A sample weighing 70.0 g of the oligomer prepared in Example III was blended with 26.0 g of tetrahydrofurfuryl acrylate to produce a solution. To the solution was added 3.0 g of 1-hydroxycyclohexylphenyl ketone and 0.5 each, of the sebacate stabilizer and the hydrocinnamate stabilizer described in Example 2. The solution exhibited a viscosity of 4370 millipascal-seconds. The solution was subsequently cured by ultraviolet irradiation to produce a polymer. The polymer proved to be immediately self-extinguishing in horizontal and vertical flammability tests. Only minimal smoke was observed during testing. The polymer has a clear, straw appearance and was flexible.

#### Example V

An oligomer was prepared by first reacting 92.56 g of 2-hydroxyethyl acrylate with 208.22 g of toluene diisocyanate in the presence of 0.15 g of phenothiazine as an inhibitor, at 25° to 40°C in an atmosphere of dry air. To this mixture was added 197.21 g of FYROL<sup>™</sup> 6 and 214.42 g of tripropylene glycol diacrylate, which served as a reactive diluent. The mixture was heated to 90°C with stirring to complete the reaction. The resulting oligomer was clear and amber in color, and has a viscosity greater than 1 million millipascal-seconds.

#### Example VI

A sample weighing 68.0 g of the oligomer

- 12 -

prepared in Example V, was blended with 28.0 g of diethyleneglycol diacrylate to produce a solution. To the solution was added 3.0 g of 1-hydroxycyclohexylphenyl ketone, 0.5 g of bis(1,2,2,6,6-pentamethyl-4-  
5 piperidinyl)sebacate and 0.5 g of triethylene glycolbis[3-(3'-tert-butyl-4'-hydroxy-5'-methylphenyl) propionate]. The solution exhibited a viscosity of 7200 millipascal-seconds.

Thereafter, the solution was cured by  
10 ultraviolet radiation to produce a polymer. The polymer was amber in color and clear.

Analyses indicated that the polymer quickly self-extinguished during horizontal and vertical flammability tests. A film of the polymer was observed to be relatively  
15 hard and brittle.

#### Example VII

The procedure of Example VI was performed again, except that 3.0 g of a blended photoinitiator was utilized  
20 in place of the 1-hydroxycyclohexylphenyl ketone. The blended photoinitiator contained equal parts of 2-hydroxy-2-methyl-1-phenylpropane-1-one and 2,4,6-(trimethylbenzoyldiphenylphosphone) oxide. The solution exhibited a viscosity of 7400 millipascal-seconds.  
25 Ultraviolet irradiation produced a clear polymer of amber color. A film of the polymer was relatively hard and brittle. The polymer self-extinguished quickly in horizontal and vertical flammability tests.

#### 30 Example VIII

A sample weighing 58.0 g of the oligomer prepared in Example I was blended with 30.0 g of trimethylol propane ethoxylated triacrylate and 8.0 grams of diethylene glycol diacrylate to produce a solution. To  
35 the solution was added 3.0 g of 1-hydroxycyclohexyl phenyl ketone as a photoinitiator. Additionally, 0.5 g each of the stabilizers bis(1,2,2,6,6-pentamethyl-4-

- 13 -

piperidinyl)sebacate and triethylene glycol bis[3-(3'-tert-butyl-4'-hydroxy-5'-methylphenyl)propionate] were blended into the solution. The solution exhibited a viscosity of 3240 millipascal-seconds and a density of 1.199 grams per cubic centimeter. Thereafter, the solution was cured by ultraviolet radiation from a Fusion Systems "D"-lamp at a dose of 1.0 joule per square centimeter to produce a polymer.

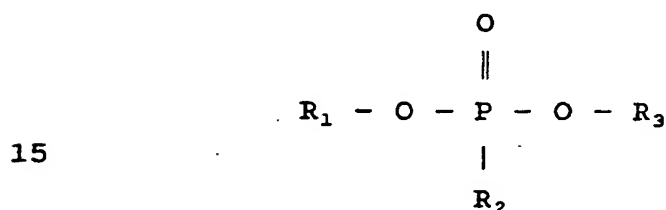
The cured polymer exhibited a clear appearance and a light straw color. It was determined that the polymer had a tensile strength of 9.9 megapascals, an elongation of 14 percent and a modulus of 130 megapascals. Both horizontal and vertical flammability tests demonstrated that the polymer was self-extinguishing and produced minimal smoke. The polymer was rated as 94 HB using Underwriter's Laboratory test method for horizontal flammability UL-94 and V-O using vertical flammability test UL-94.

Preferred aspects of the invention have been described to better communicate the invention. However, the scope of the invention is intended to be as broad as the appended claims will allow.

Examples I, III and V demonstrate that radiation curable oligomers that are essentially free of halogens can be prepared by oligomerizing and end-capping a blend of a phosphonate polyol and a diisocyanate. Example II, IV, VI, VII and VIII prove that a relatively flame retardant halogen-free polymer can be prepared by radiation curing of the composition within the scope of the present claims.

C L A I M S

1. A radiation curable composition suitable for  
producing a flame retardant polymer, which comprises:  
5 an oligomer that is the reaction product of a  
polyisocyanate and a phosphonate polyol, said  
oligomer being end-capped by at least one  
monohydroxyfunctional compound with ethylenic  
unsaturation; and an organic monomer; said polyol  
10 having the formula;

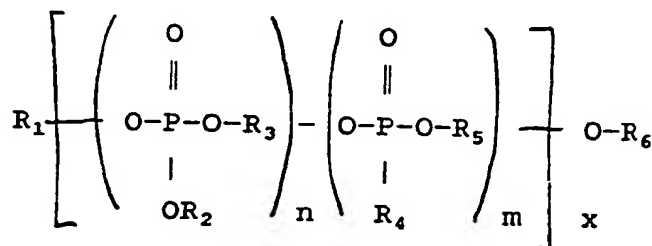


- wherein  $\text{R}_1$  and  $\text{R}_3$  are independently  $\text{C}_1$  to  $\text{C}_{18}$  alkyl or  
aryl; and  $\text{R}_2$  is polyhydroxyalkyl, polyhydroxyaryl,  
20 polyhydroxyalkylaminoalkyl, polyhydroxyarylamino-  
alkyl, polyhydroxyalkylaminoaryl or polyhydroxyaryl-  
aminoaryl having from 1 to 18 carbon atoms inclusive.
2. The composition of claim 1 wherein said  
polyisocyanate is selected from the group consisting  
25 of toluene diisocyanate, trimethylhexane  
diisocyanate, dicyclohexylmethane diisocyanate,  
isophoronediiisocyanate, diphenylmethane diisocyanate,  
hexamethylene diisocyanate, phenylene diisocyanate,  
and biphenyl diisocyanate.
- 30 3. The composition of claim 1 wherein  $\text{R}_1$  and  $\text{R}_3$  are  
ethyl.
4. The composition of claim 1 wherein  $\text{R}_2$  is N,N-bis(2-  
hydroxyethyl) aminomethyl.
5. The composition of claim 1 wherein said organic  
35 monomer is selected from the group consisting of  
tetrahydrofurfuryl acrylate, ethoxyethoxyethyl  
acrylate, diethyleneglycol diacrylate,



trimethylolpropane ethoxylate triacrylate, methoxyethyl acrylate and hydroxy caprolactone acrylate.

6. The composition of claim 1 wherein said monohydroxy compound with ethylenic unsaturation is 2-hydroxyethyl acrylate.
7. A radiation curable composition suitable for producing a flame retardant polymer, which comprises: an oligomer that is the reaction product of a polyisocyanate and a phosphonate polyol, said oligomer being capped by at least one monohydroxy functional compound with ethylenic unsaturation; and an organic monomer; said polyol being the reaction product of dimethyl methylphosphonate, phosphorus pentoxide, ethylene oxide and water in a molar ratio of about 2:2:8:1, respectively.
8. A radiation curable composition suitable for producing a flame retardant polymer, which comprises: an oligomer that is the reaction product of a polyisocyanate and a phosphonate polyol, said oligomer being capped by at least one monohydroxy functional compound with ethylenic unsaturation; and an organic monomer; said polyol having the formula:



wherein  $R_1$ ,  $R_2$ ,  $R_4$  and  $R_6$  are each independently selected from the group consisting of alkyl, aryl, poly (alkylene oxide) polyhydroxyalkyl, polyhydroxyaryl, polyhydroxyalkylaminoalkyl, polyhydroxyarylaminoalkyl, polyhydroxyalkylaminoaryl and polyhydroxyarylaminoaryl;  $R_3$  and  $R_5$  are each independently selected from the group consisting of

- 16 -

- alkylene and arylene; m and n are each independently an integer from 0 to 10 inclusive, provided that at least one of m and n is 1 or more; and x is 1 to 100.
9. The composition of claim 8 wherein said monohydroxy compound with ethylenic unsaturation is 2-hydroxyethylacrylate.
10. The composition of claim 8 wherein  $R_3$  and  $R_5$  are ethylene.
11. The composition of claim 8 wherein  $R_4$  is methyl.
12. The composition of claim 8 wherein said polyisocyanate is selected from the group consisting of toluene diisocyanate, trimethylhexanediisocyanate, dicyclohexyl methane diisocyanate, isophorone diisocyanate, diphenylmethane diisocyanate, hexamethylene diisocyanate, phenylene diisocyanate and biphenyl diisocyanate.
13. The composition of claim 8 wherein said organic monomer is selected from the group consisting of diethyleneglycol diacrylate, tripropyleneglycoldiacrylate, hexanediol diacrylate, tetrahydrofurfurylacrylate and trimethylolpropane ethoxylate triacrylate.
14. A substrate that is coated with the composition of claim 1, which is cured.
15. A substrate that is coated with the cured composition of claim 8, which is cured.
16. A group of optical fibers having a matrix made from the cured composition of claim 1.
17. A group of optical fibers having a matrix made from the cured composition of claim 8.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/NL 94/00155A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08G18/38 C08G18/67

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 657 968 (GOEL) 14 April 1987 see column 1, line 42 - column 3, line 9; claims 1-5; example 3 ---	1-13
X	US,B,364 910 (KÜHN) 28 January 1975 see column 2, line 1 - column 9, line 52; claims 1-18 ---	1-13
X	CHEMICAL ABSTRACTS, vol. 102, no. 2, 14 January 1985, Columbus, Ohio, US; abstract no. 7701n, 'FIRE-RESISTANT PHOTOSENSITIVE RESIN COMPOSITIONS' page 45 ;column 2 ; see abstract & JP,A,59 149 917 (HITACHI) 28 August 1984 ---	1-13
A	US,A,5 175 228 (WANG ET AL) 29 December 1992 -----	

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

11 November 1994

Date of mailing of the international search report

28. 11. 94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Bourgonje, A

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/NL 94/00155

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4657968	14-04-87	NONE	
US-B-364910		NONE	
JP-A-59149917	28-08-84	NONE	
US-A-5175228	29-12-92	CA-A- 2084181	10-06-93
		EP-A- 0546771	16-06-93
		JP-A- 5247431	24-09-93
		US-A- 5340901	23-08-94
		US-A- 5354609	11-10-94